

J.D. THORNTON.

Department of Chemical Engineering, The University,
Newcastle upon Tyne, England.

1.0. Introduction.

Although numerous investigations have been published dealing with the effects of electrical discharges upon chemical reactions, most of the work is fragmentary in the sense that even now no clear picture has emerged of the relative importance of discharge characteristics and reactor geometry upon the reaction yield. This is largely because no systematic studies have been undertaken with a fixed reaction system covering a reasonably wide range of discharge conditions and reactor configurations. Furthermore most of the published work has been concerned with laboratory-scale investigations so that, with the possible exception of ozone synthesis, little or no attention has been paid to the chemical engineering problems involved in gas phase electrosynthesis. This is no doubt consequent upon the low yields obtained in many laboratory studies and is unfortunate in that a proper application of the engineering factors affecting the reactor efficiency could, in many cases, lead to considerably improved reaction yields.

Whereas physical chemistry is usually concerned with the individual kinetic steps contributing to a particular reaction scheme, chemical engineering is concerned with the translation of the laboratory reaction to a full scale continuous process wherein the desired reaction product is produced at the lowest capital and operating costs. In the case of gas discharge synthesis, these financial criteria imply that the reactor should have three highly desirable characteristics:

- (a) The energy yield (Gms. product per Kw.Hr.) should be high.
- (b) The conversion per pass should be high.
- (c) The reactor should be selective for the desired product, i.e. side reactions with their consequent wastage of material and energy should be minimised.

In practical terms, it is not necessary to have a detailed step by step knowledge of the reaction kinetics in order to design the reactor, so long as an empirically determined rate equation is available which adequately describes the influence of the operating variables upon the net rate of reaction. Clearly a more informed approach to the design problem is possible when fundamental data are available but this is seldom the case at the design stage.

Assuming that the electrons in a discharge are able to excite the reactant molecules, it is possible that many of the low product yields hithertoreported may be attributed to one or more of the following factors:

- (a) The use of unsuitable reactor geometries in which a sizeable fraction of the reactant by-passes the discharge zone.
- (b) The use of non-optimum discharge conditions in which the average activation cross-section for the desired reaction is low.
- (c) The use of inappropriate residence times or residence time distributions of the reactants and products.
- (d) The presence of parallel reactions which compete for the reactant and the occurrence of rapid reverse and degradation (or consecutive) reactions which destroy the primary product.

It is with these aspects of gaseous electrosynthesis that the present paper is concerned, since it is possible that many of these effects can be minimised by proper consideration at the reactor design stage.

2.0 Reactor Classification.

It is useful to consider initially the basic reactor geometries that can be employed in a continuous-flow reaction system. Although no formal reactor classification has hitherto been proposed, the electrode configuration and direction of

flow of the reactant gas stream can be made the basis of a convenient system of classification. Thus the electrodes may consist of parallel plates, co-axial cylinders or a pair of points whilst the gas flow may be parallel or at right angles to the plane of the discharge. Figure 1 shows in diagrammatic form the 4 various electrode and flow arrangements on the basis of this classification. Parallel flow in parallel plate and coaxial electrode reactors necessitates the use of porous electrodes through which the gas phase flows as shown in Figures 1.1 and 1.2. On the other hand, the commoner cross-flow arrangements shown in Figures 1.4, 1.5 and 1.6 usually employ impervious metal electrodes, there being no necessity for the reactants to flow through the electrodes themselves. The usual parallel/point and cross-flow/point reactors are depicted in Figures 1.3 and 1.7 respectively.

The distinction between parallel-flow and cross-flow is not an academic one by reason of the non-uniform nature of the electric field in many of these reactor arrangements. In most of the laboratory investigations reported in the literature, the areas of the electrodes are small and little or no attempt has been made to minimise edge effects by the use of suitable electrode profiles. The field intensity is therefore a function of position in the inter-electrode gap. Furthermore the use of coaxial geometries where the respective electrode radii are very different also gives rise to highly non-uniform fields in the vicinity of the central electrode. It follows therefore that the overall activation effects might well be different in the parallel/parallel and cross-flow/parallel systems in Figures 1.1, 1.4 and 1.5. In the former case, molecules traversing a centre-line path will encounter electrons of different energies to molecules following a peripheral path whilst, in a cross-flow reactor, all the molecules encounter electrons with a wide spectrum of energies. In coaxial reactors, the position is further complicated by virtue of the non-uniform field associated with the central electrode. Thus in Figures 1.2 and 1.6 not only is there a transverse field variation but there is also an axial variation as the molecules approach the bottom and top planes of the outer electrode.

Such considerations are purely speculative at the present time because no experimental data are available which would enable a direct comparison of reactant conversions for parallel and cross-flow systems to be made for the same reactants under similar conditions. Nevertheless these factors must be born in mind when interpreting the influence of reactor geometry on a quantitative basis.

Coaxial electrode systems in which the reactant flows through the annular space between the two electrodes have an advantage in that all the reactant molecules must pass through the discharge. There is therefore no by-passing and subject to suitable electron energies, there will be a high level of activation in the gas phase. Such conditions are difficult to achieve in parallel plate arrangements unless the reactant is introduced at the centre of one of the electrodes as in Figure 1.4. Much work has been reported with point electrode systems such as those illustrated in Figures 1.3 and 1.7 and here it is difficult to see how by-passing of the discharge can be avoided. Furthermore the flow pattern within the reactor is also dependent upon the turbulence level so that changes in the gas flowrate will almost certainly be accompanied by corresponding changes in the fraction of the gas stream by-passing the discharge zone.

All the reactor systems discussed so far can be described as homogeneous in the sense that only a single, gaseous, phase is present in the reactor. In many instances, however, it is advantageous to remove one or more products of reaction as rapidly as possible in order to minimise subsequent reactions which would adversely affect the primary reaction yield. A convenient method of achieving this involves the introduction of a second phase into the discharge zone in the form of a liquid absorbent (6) or fluidised solid adsorbent (12). In principle a second phase can be introduced between any of the electrode arrangements shown in Figure 1. This modification gives rise to a second series of reactor systems which will be referred to subsequently as heterogeneous reactors.

3.0 Nature of the Electrical Discharge.

For optimum reactor performance it is necessary to ensure that the reactants

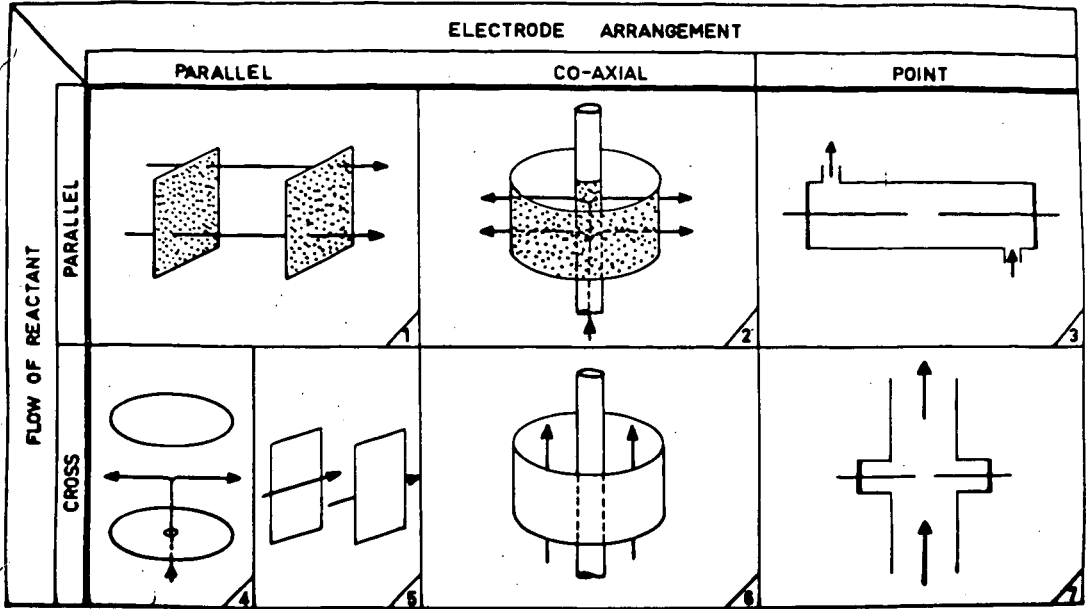


Fig.1. Basic reactor geometries.

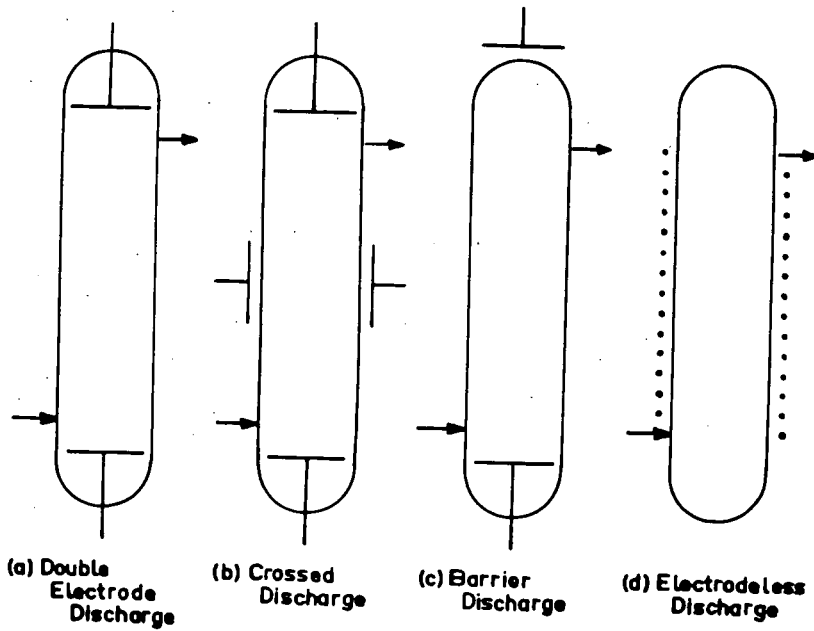


Fig.2. Diagrammatic electrode arrangements for various discharge conditions.

have suitable residence times in that part of the discharge zone where activation is most favoured. In this connection it will be recalled that the relative rate of ammonia synthesis from its elements has been shown to be greatest in the region of the cathode potential drop (λ) whilst in the case of hydrazine synthesis from ammonia, the significant fraction of the discharge is the positive column region (4). In theory, it is desirable to be able to predict the discharge conditions necessary for optimum conversion in any particular reaction; in practice however, this is not yet possible. This is because in the past it has been customary to describe discharges in general terms such as glow, arc or silent discharges without regard to the local or point properties existing in different parts of the discharge zone. Since there is a gradual transition between our regime and the next, qualitative descriptions of this type are not of great value in interpreting reaction rate data. Any fundamental correlation of rate data with discharge characteristics would involve not only a knowledge of the concentrations and energy distributions of the various particle species present in the discharge space, including electrons, but also an understanding of the way in which the probability of excitation varied with electron energy. A typical example of the way in which the degree of excitation is dependent upon electron energy is shown in Figure 3 which depicts total cross-section curves for argon and neon (5). The cross-section for an m n type transition by electron collision is zero when the electron energy is less than the energy required to raise a valency electron of an atom from the m^{th} to the n^{th} level, but increases with electron energy to a maximum after which any further increase in electron energy is accompanied by a decrease in the value of the total cross-section. There is therefore an optimum value of the electron energy corresponding to the maximum cross section for the process under consideration. It is the lack of data of this type together with a knowledge of the reactive species present in the discharge that makes it difficult to correlate reaction rates with discharge parameters for systems of engineering interest.

Nevertheless despite the absence of fundamental information relating to the activation characteristics of discharges, one or two general observations can be made with regard to the nature of the discharges commonly employed. All the reactor geometries discussed so far, and illustrated diagrammatically in Figure 1, employ the same type of discharge in the sense that both electrodes are located within the reactor and are therefore in contact with the reactant gas. This class of discharge in which electrons pass freely between the two electrodes is represented schematically in Figure 2a. An alternative type of discharge which has been used frequently is the so called barrier discharge shown diagrammatically in Figure 2c. Here one of the electrodes is separated from the gas phase by means of a dielectric barrier such as quartz so that the reactor may be looked upon as a capacitive and resistive load in series. In practice a dielectric barrier may be employed in conjunction with any of the reactor geometries shown in Figure 1. This arrangement has the advantage of providing a more uniform type of discharge which is current limited so that the build up of spark or arc type discharges is avoided. If this principle is carried to its logical conclusion, both electrodes may be isolated from the reactant gas and molecular excitation set up by applying a high frequency potential to the external electrodes or by induction from an external conductor carrying a high frequency current. (Figure 2d.) This type of "electrodeless" reactor has not been mentioned in the classification discussed above but is of interest since in the absence of metal electrodes in the gas phase, the degree of dissociation of the gas and therefore the concentration of atoms would be expected to be high (10). The high concentration of atomic species in such discharges is evidenced by the afterglow phenomena frequently encountered in electrodeless systems.

One type of electrodeless system which might well prove of interest in electrosynthesis is the microwave discharge. Here the degree of activation can be high (9) and it has been reported that the atomic yields in hydrogen, nitrogen and oxygen are approximately ten times greater than the yields of atoms and radicals in low frequency and direct current discharges at the same field strength and pressures. From the engineering point of view, microwave systems have the added advantage

that they can be sustained at higher pressures but on the other hand the detailed economics still require evaluation.

The crossed discharge arrangement shown in Figure 2b comprises a low frequency discharge at right angles to one of high frequency. The discharge zone itself is said to be characterised by a low energy density and to result in unexpectedly high activation of the reactants and relatively high yields of the reaction products (3). These claims have not however been confirmed by recent work in these laboratories in which methane was subjected to a crossed discharge at 31 mm.Hg pressure. The reactor consisted of a 15 mm. internal diameter glass tube fitted with two pairs of 3 mm. diameter stainless steel electrodes arranged at right angles. The percentage decomposition of methane was observed using a 0.91 Mc/s high frequency discharge, a 50 c/s low frequency discharge and combinations of high and low frequency discharges simultaneously. Figure 4 shows some typical data plotted in the form % methane decomposed versus % H.F. power for a series of runs at constant total power. The methane flowrate was constant throughout at 93 cc/minute at N.T.P. These results confirm the general trend whereby an increase in discharge power is accompanied by an increase in the percentage decomposition of the methane but on the other hand do not substantiate the claim made for the higher activating effect of the crossed discharge. Had this been the case, the curves shown in Figure 4 would have exhibited maxima whereas, in fact, the observed methane decomposition at constant total power increased steadily with increasing percentage of H.F. power. In this particular case, there is therefore no advantage in the use of crossed discharges and the characteristics claimed by Cotton still remain to be confirmed.

4.0 Product Selectivity and Residence Time Considerations.

In the simple plug flow reactor, the conversion (x) obtained is related to the residence time (τ) by the expression:

$$\tau = \int_0^x \frac{dx}{U_p \cdot r}$$

where U_p and r are the molal volume of the reacting mixture and the reaction rate respectively. If the reaction is one which can only take place under the influence of an electrical discharge, then the residence time refers to the time spent by the reactants in the discharge zone itself. If however subsequent reactions involving the primary reaction products are possible outside the discharge zone, these will usually proceed at a different rate and must be taken into account separately in analysing the overall performance of the reactor system.

If the reaction rate (r) could be written in terms of the concentrations of the reactants and a rate constant (k) which in turn was dependent upon the discharge characteristics, then in principle it would be possible to integrate the above expression for any set of discharge conditions and compute the residence time for any desired conversion. In practice however this is seldom possible because the functional relationship between the reaction rate and the discharge characteristics is unknown.

Discharge reactions are frequently complicated by reason of the interactions between the atomic, molecular, ionic and free radical species present. Moreover because of the wide range of species present, reactions are rarely simple in the sense that only one primary reaction product is produced. Competing parallel, consecutive and degradation reactions are often present, the net result of which is to produce a wide spectrum of reaction products. One of the key problems at the present time therefore is how to design reactors in which unwanted side reactions are reduced to a minimum. There is no clear-cut answer to this problem as yet, but an examination of some of the more elementary types of reactions such as those listed in Table I indicates a promising method of approach.

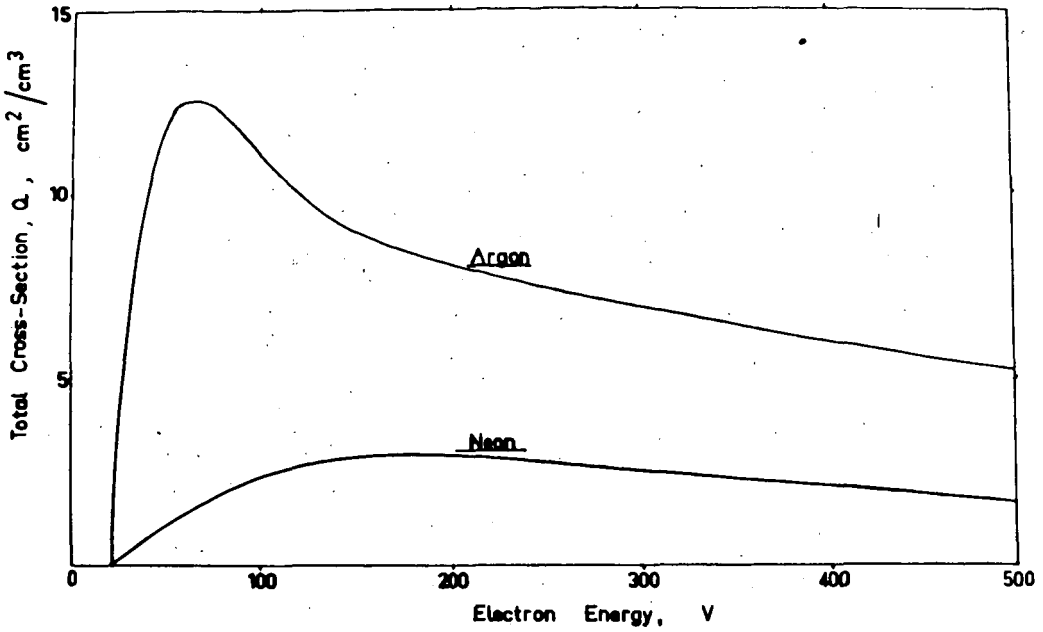


Fig.3. Typical Cross-Section versus Electron Energy Curves.

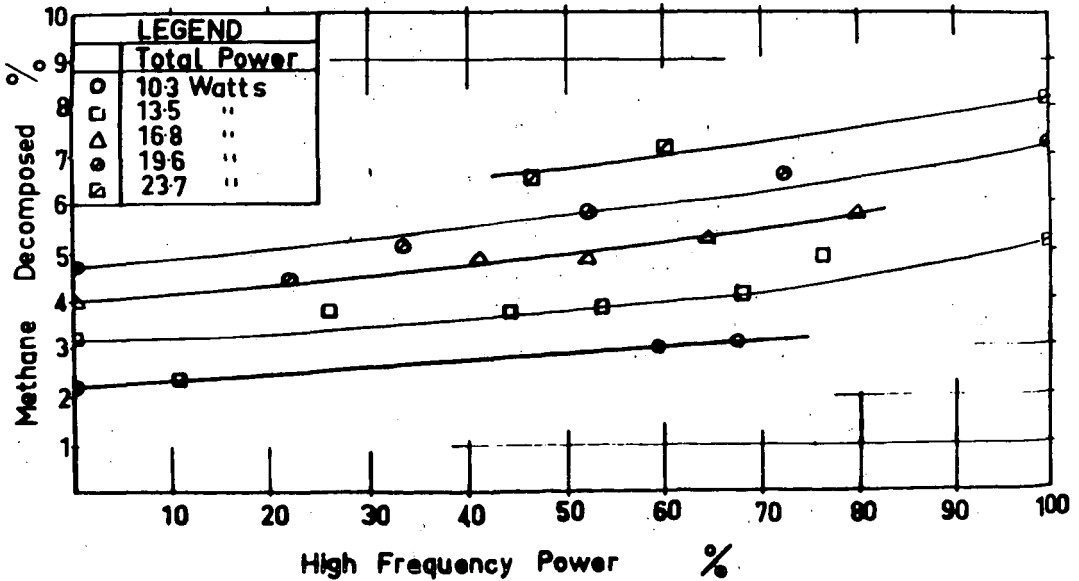


Fig.4. Effect of a Crossed Discharge on % Methane Decomposition.

TABLE I
Examples of Elementary Reactions.

Consecutive Reactions	$A + B \rightarrow C$ $A + C \rightarrow D$
Polymerisation Reactions	$A + A \rightarrow B$ $A + B \rightarrow C$ $A + C \rightarrow D$
Parallel Reactions	$A + B \begin{matrix} \rightarrow C \\ \rightarrow D \end{matrix}$
Reversible Reactions	$A + B \rightleftharpoons C + D$
Degradative Reactions	$A + B \rightarrow C \rightarrow D \rightarrow E$

In all the reactions listed in Table I it is assumed that C is the preferred product. Intermediate steps involving excited species are omitted so that the equations merely represented the overall stoichiometry of the various situations. If therefore product C is being produced from reactants A and B and a second (consecutive) reaction is present which destroys C, then the rate of the second reaction can be reduced by maintaining the concentration of C at a low value. Since the primary reaction responsible for the formation of C should, on economic grounds, proceed as rapidly as possible, the only way of maintaining a low product concentration is to remove C from the discharge zone as rapidly as it is formed. The methods by which this can be achieved will be discussed further below.

The same principles apply to the other reactions in Table I. Thus in the case of polymerisation reactions, the molecular weight of the product can be controlled by selective removal of certain constituents from the discharge. If product B is preferred, then further polymerisation can be minimised by rapid removal of B. If on the other hand, the higher molecular weight product C is required, B is allowed to remain in the discharge and C is selectively removed. It frequently happens that the product yield is limited by reverse and parallel reactions. In the latter case, C can be produced in preference to D by selective removal of C. In the former instance, any yield limitations imposed by equilibrium considerations can be overcome by rapid removal of C so that the equilibrium is displaced almost entirely in favour of products.

Similar reasoning shows that in the case of degradative reactions, product C can be produced in preference to D or E provided that C is removed rapidly enough from the activating influence of the discharge.

A number of methods are available for the rapid removal of a particular component from the discharge zone, namely:

- (1) Quenching the reaction at low temperatures and freezing out the product (2)
- (2) Absorbing the desired product selectively in an inert liquid absorbant (6)
- (3) Adsorbing the desired product in a fluidised bed of solid adsorbent (12).
- (4) By using a low residence time in the discharge zone. This may be achieved either by high gas flowrates or by using a pulsed discharge technique. These are all devices which reduce both the product concentration and residence time in the gas phase and so minimise product losses through subsequent reactions.

Methods (1) - (3) are means of controlling selectively the residence time and concentrations of certain specific products in the discharge and a choice can only be made between them in the light of the physical properties of the various constituents of the gas phase. The fourth method, which does not discriminate between the concentrations or residence times of reactants and products, can only be evaluated when the relative rates of the competing reactions are known. Of the various techniques available, simultaneous reaction and absorption in a heterogeneous reactor (method 2) opens up interesting possibilities for producing economic

yields of many chemical products where hitherto the overall yield has been restricted by decomposition reactions. The theoretical analysis of such systems is however extremely complex and even if the kinetics of the process were fully understood, it is doubtful if the absorption rate into the liquid phase could be predicted with any degree of certainty because of complications arising from dielectrophoretic stirring of the liquid. If the liquid phase is polarizable the electrical forces in a non-homogeneous field will cause polar molecules to move towards regions of maximum non-homogeneity. Any turbulence thereby set up within the liquid phase will enhance the rate of gas absorption but at the same time render the prediction of mass transfer coefficients extremely uncertain. From a practical point of view, such effects are desirable insofar as it is important that the rate of absorption of the product should be high compared with its rate of production by synthesis.

Some illustrations of the factors discussed are of interest at this stage and Figs. 5 and 6 show how the molecular weight of the product is influenced by residence time in the case of consecutive type reactions involving methane as the reactant. Figure 5 shows how the higher molecular weight product, in this case propane, is favoured by longer residence times in the discharge (11). These data were obtained at 80 mm Hg pressure in a cross-flow/coaxial reactor with a 1.60 mm. thick quartz barrier adjacent to the inside surface of the outer electrode. The relevant electrode diameters were 17 mm and 3 mm respectively and the power density was 0.05 Kw/cc throughout. Figure 6 shows the effect of longer residence times on the higher molecular weight fraction from methane at a pressure of 10 mm Hg and again the molecular weight of the product is strongly dependent on residence time (7).

In the discharge synthesis of hydrazine from ammonia, it has been suggested (4)(1) that the hydrazine can be subsequently destroyed by further electron excitation or by reaction with atomic hydrogen produced in the primary electron bombardment of ammonia. If therefore the concentration and residence time of the hydrazine in the discharge be reduced, degradative reactions should be minimised and the yield increased correspondingly. That this is the case can be seen from Figures 7 and 8. The arrangement of the cross-flow/coaxial reactor employed in these runs is shown in Figure 9. The reactor tube was made from 1.60 mm. thick quartz tubing which constituted the dielectric barrier and was 28.6 mm. O.D. The inner electrode consisted of a perforated stainless steel drum 19 mm O.D. which was mounted on a coaxial shaft so that it could be rotated at high speed. A liquid absorbent, in this case ethylene glycol, was fed to the drum so that, as the latter rotated, the glycol was forced through the drum perforations into the discharge annulus in the form of a fine spray. The data shown in Figure 7 were obtained at an average power density of 0.044 Kw/cc and illustrate the fact that not only can the energy yield of hydrazine be increased by reducing the gas residence time but that a further substantial increase in yield can be obtained if the hydrazine is rapidly removed from the discharge by selective absorption (13).

The data shown in Figure 8 in which the energy yield is plotted versus the discharge duration for a constant gas flowrate were obtained in a cross-flow parallel plate reactor using a pair of electrodes each measuring 12.5 x 6.3 mm. and located 11 mm. apart. In these runs the average power density was 0.01 Kw/cc using a pulsed D.C. discharge, the pulse duration ranging from 12 to 130 microseconds. Under these conditions, the effective residence time of the reactant and products was no longer dictated by the gas flowrate but by the pulse duration. This technique is therefore a device for securing very low residence times without the inconvenience of high gas velocities. Again the data are in agreement with previous results in that the lower residence times favour higher energy yields because of the smaller loss of hydrazine through reverse and consecutive reactions. It is interesting to note that an alternative technique whereby atomic hydrogen is converted to less reactive molecular hydrogen through the agency of a platinum catalyst has also shown increased yields of hydrazine (4).

It has been assumed so far that the reactant flows as a coherent plug through the discharge. This concept of plug-flow is only an approximation at

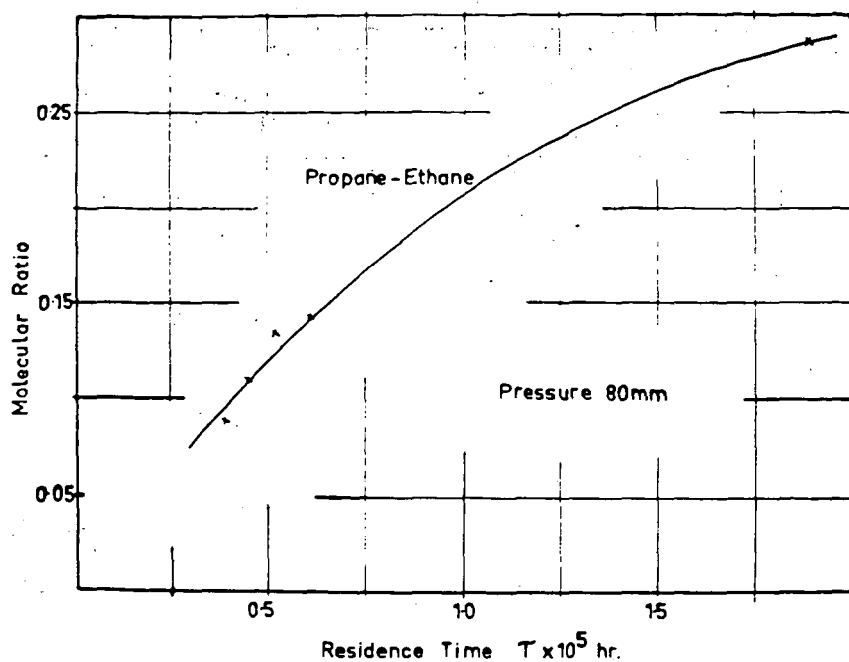


Fig.5. The effect of residence time on propane-ethane yield from methane.

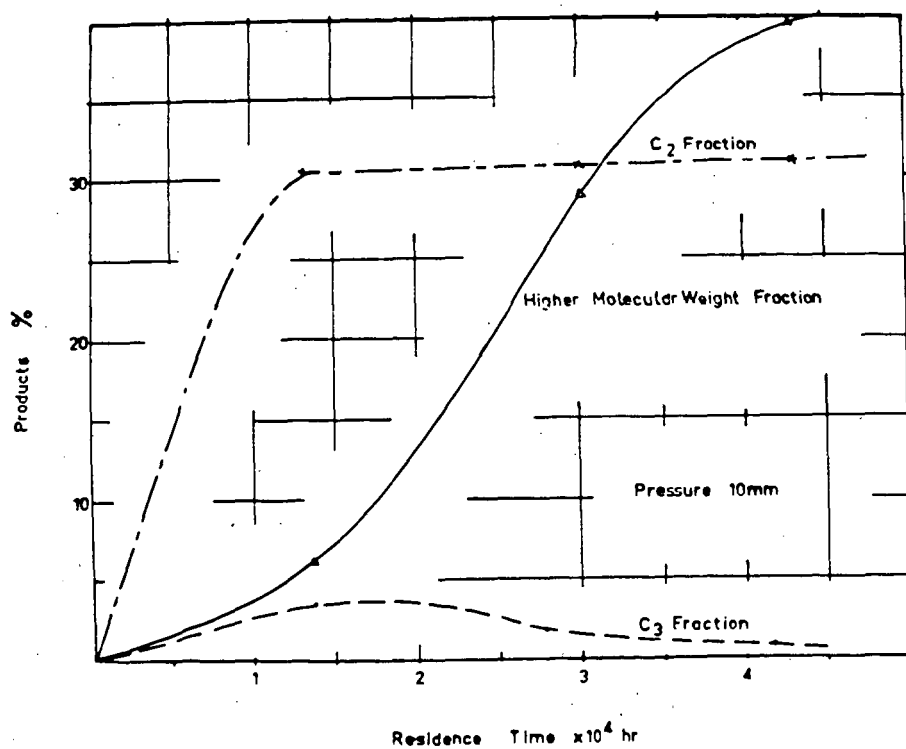


Fig.6. The effect of residence time on the yield of higher molecular weight fraction from methane.

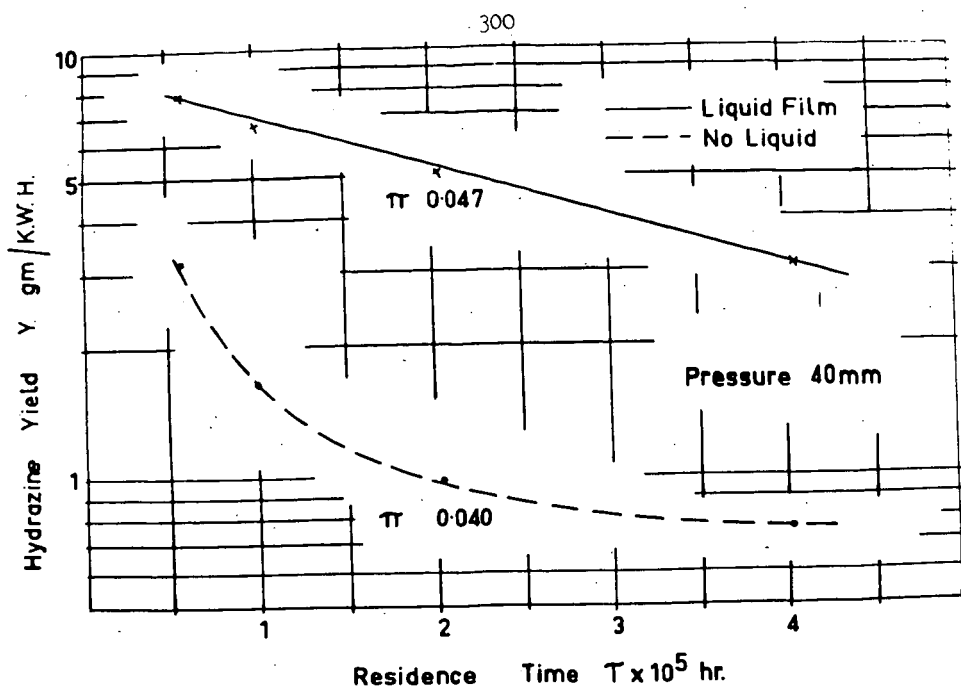


Fig.7. The effect of residence time and absorbent on hydrazine yield from ammonia.

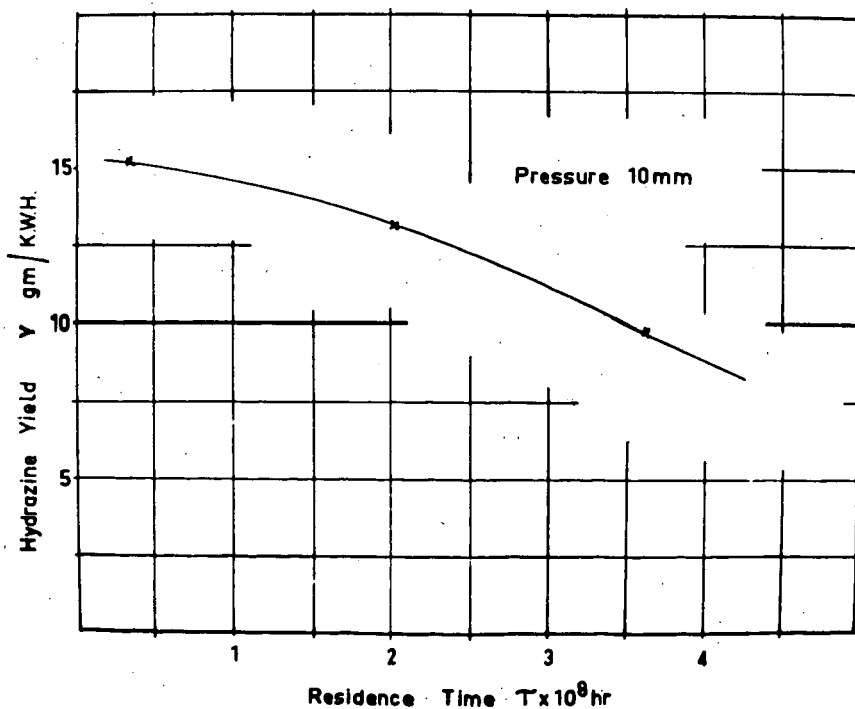


Fig.8. The effect of residence time on hydrazine yield from ammonia when residence time is dictated by the discharge waveform characteristics.

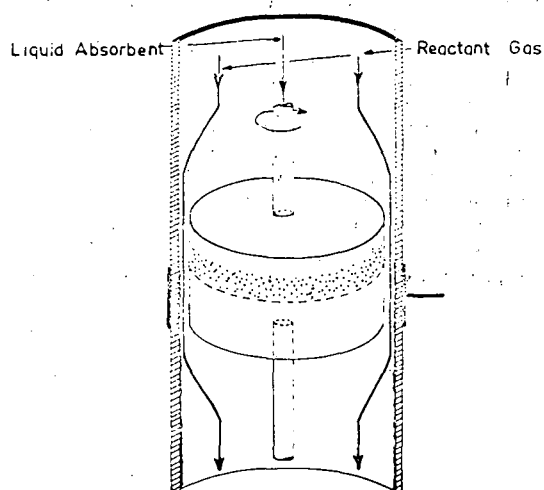


Fig.9. . Arrangement of the differential reactor for hydrazine synthesis from ammonia.

the best and in many practical situations considerable divergences are observed between the residence time (τ) calculated from

$$\tau = \int_0^x \frac{dx}{U_z \cdot r}$$

and the residence time observed in practice for the same conversion. Such discrepancies result from the velocity profile of the gas as it passes through the reactor; molecules adjacent to the wall will have a lower velocity than molecules travelling along an axial path and as a result there will be a distribution of residence times. The effect of such a distribution can be serious in the case of polymerisation-type reactions where a wide spread in residence-times is often accompanied by a corresponding spread in the molecular weights of the products. If therefore a product is required with a relatively narrow molecular weight distribution, steps must be taken to ensure that the distribution of residence times is correspondingly small. One way of achieving this is to promote rapid mixing in the reactor by the use of suitably designed baffles so that each element of gas spends approximately the same time in the discharge.

Acknowledgements.

The author is indebted to a number of his colleagues and to Dr. C.A.Walley of the Department of Electrical Engineering for many helpful discussions.

References.

- (1) Andersen W.H., Zwolinski B.J., Parlin R.B., Ind.Eng.Chem., 1959, 51, (4), 527.
- (2) Brewer A.E., Westhaver J.W., J.Phys.Chem., 1929, 33, 883 (Cf. also J.Phys.Chem. 1930. 34, 153)
- (3) Cotton W.J., Trans.Electrochem.Soc., 1947, 91, 407, 419.
- (4) Devins J.C., Burton M., J.Amer.Chem.Soc., 1954, 76, 2618.
- (5) Howatson A.M., "Introduction to Gas Discharges" (Pergamon Press, 1965).
- (6) Imperial Chemical Industries, U.K. Patents 948,772; 958,776; 958,777; 958,778; 966,406 (all 1964).
- (7) Kraaijveld Von H.J., Waterman J.I., Brennstoff-Chemie, 1961, 42, (12), 369.
- (8) Llewellyn-Jones F., "Ionisation and Breakdown in Gases", (Methuen & Co. Ltd. 1966).
- (9) McCarthy R.L., J.Chem.Phys., 1954, 22, 1360.
- (10) Miyazaki, Takahashi, Nippon Kagaku Zasshi, 1958, 78, 553.
- (11) Sergio R. Unpublished Work, University of Newcastle upon Tyne. England.
- (12) Thornton J.D., Chem.Processing, 1966, XII (2), S6.
- (13) Thornton J.D., Charlton W.D., Spedding P.L., "Hydrazine Synthesis in a Silent Electrical Discharge" (to be published).